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IMPROVEMENT OF THE COMPOSITIONS AND PROPERTIES OF GRAY CERAMIC PIGMENTS

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A comparative analysis of the optical and color characteristics of well-known gray ceramic pigments is performed and the effectiveness of different opacifying components in them is evaluated. Gray pigments with stable optical indicators are synthesized using open hearth slag. It is shown that zirconium compounds, characterized by inertness with respect to the coloring components in the pigment and by high resistance to dissolution by glass melts, are shown to be effective opacifiers for obtaining these pigments.

Key words: ceramic pigments, opacifiers, coloring components, open hearth slag, color, crystal phase composition, optical indicators, glaze coatings.

Both chromatic and achromatic pigments, specifically, gray pigments, which are synthesized in different systems using expensive commercial raw materials, are quite widely used to impart color to glass coatings and decorate ceramic articles. Obtaining such pigments with stable optical and color indices is a difficult scientific and technical problem, whose solution is largely determined by picking the proper ratio of the coloring components, which gives the black color component, and by the concentration and nature of the opacifier introduced, which determines the white component.

For this reason research aimed at using unconventional (secondary) raw material to lower the materials costs of obtaining gray ceramic pigments is topical. In addition, it is of interest to evaluate the effectiveness of different opacifiers as components in such pigments.

The conventional opacifiers in the synthesis of gray pigments are tin, zirconium and titanium dioxides, which possess high refractive indices [1, 2].

It is well-known that corrosion of ceramic pigments by glass melts is unavoidable in the course of firing of glaze and enamel coatings [3]. The final color is determined by the resistance of the color-carrying phases of the pigments to attack by high-temperature melts of glazes and enamels.

The largest users of ceramic pigments are producers of glazed ceramic tile, for which fritted glazes are used. For this reason we synthesized gray ceramic pigments, well-known in the literature [2, 4 – 9], using commercial raw material to reveal their resistance to melts of transparent fritted glaze (INTERKERAMA, JSC, Dnepropetrovsk) intended for deposition on ceramic tile for interior wall facings. The compositions and properties of the ceramic pigments and glass coatings containing them are presented in Table 1. The experimental pigment-containing glass coatings were fired at the maximum temperature 1100°C and then rapidly cooled. The optical measurements of the synthesized pigments and glaze coatings were conducted on a KTs-3 color comparator.

It was determined experimentally that of the ceramic pigments studied only the compositions 4l – 6l are characterized by gray color. The diffuse reflection coefficient (DRC) is in the range 19.67 – 25.51%. Such pigments contain as initial opacifiers titanium dioxide, zirconium silicate and tin dioxide. Cobalt, iron, chromium and vanadium oxides in different quantitative ratios are used to create the color effect. A high concentration of the chromophore oxides in the pigments 2l, 8l and 9l gives rise to the black color, as indicated by the low values of the DRC (9.60 – 9.96%). In the pigments 1l, 3l and 7l it is evident that the ratio between the coloring oxides and opacifying components is suboptimal, which is why brown, turquoise and light blue colors, respectively, predominate. Analysis of the data obtained for pigment-containing glaze coatings showed that none of the pigments studied promote the formation of a gray color of the glass layer. Thus, the pigments with the compositions 4l – 6l, which after firing were characterized by gray color, promoted the formation of a glass layer with gray-blue (DRC = 6.67%), gray-brown (8.81%) and gray – light-blue (14.64%) colors, respectively. The ceramic pigments 2l, 8l and 9l also are not distinguished by high resistance of the base glaze to the glass melt; these pigments were characterized by black color, which is con-

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TABLE 1. Compositions and Characteristics of Gray Ceramic Pigments and Glass Coatings with Their Applications

Index	Pigments studied								
	1l [4]	2l [5]	3l [6]	4l [7]	5l [8]	6l [9]	7l [2]	8l [2]	9l [2]
Content, wt.%:									
silicon dioxide	60.71	12.35	–	33.68	26.7	–	–	–	–
aluminum oxide	16.48	–	21.04	–	–	–	50.0	–	–
calcium oxide	0.51	–	11.78	20.96	–	–	–	–	–
magnesium oxide	0.11	11.65	–	–	–	–	–	–	–
sodium oxide	2.72	–	–	–	–	–	–	–	–
potassium oxide	9.77	–	–	–	–	–	–	–	–
zinc oxide	0.60	–	–	–	5.0	–	47.6	27.3	23.1
titanium dioxide	0.09	14.25	–	29.86	–	–	–	–	–
zirconium dioxide	–	–	–	–	39.7	–	–	–	–
tin dioxide	–	–	54.59	–	–	94.6	–	–	–
vanadium oxide (V)	–	–	–	–	–	1.4	–	–	–
iron oxide (III)	6.11	44.90	–	–	5.6	–	–	–	–
chromium oxide (III)	2.90	4.25	3.41	–	6.0	2.0	–	–	–
cobalt oxide (III)	–	5.40 (CoO)	3.41	15.50	9.0	2.0	2.4	–	–
cobalt sulfate (II)	–	–	–	–	–	–	–	27.3	30.8
iron sulfate (II)	–	–	–	–	–	–	–	45.4	38.4
potassium bichromate	–	–	–	–	–	–	–	–	7.7
boron oxide	–	–	5.77	–	–	–	–	–	–
sodium fluoride	–	7.20	–	–	8.0	–	–	–	–
Pigment characteristics									
Synthesis temperature, °C	1000	1000	1320	1150	950	1320	1150	1150	1150
Color	Gray-brown	Black	Gray-turquoise	Gray with green sheen	Intense gray with brown tinge	Gray	Pale blue	Black with blue sheen	Black
DRC, %	21.34	9.96	19.27	23.44	19.67	25.51	50.54	9.64	9.60
Characteristics of pigment-based glaze coatings*									
Color	Brown-beige	Gray-brown	Light-blue with gray sheen	Gray-blue	Gray-brown	Gray-light-blue	Very pale blue	Black-blue	Black with brown sheen
DRC, %	19.39	6.64	10.97	6.67	8.81	14.64	22.50	4.85	4.70

* Pigment was introduced into the glaze in the amount 8 parts (by weight).

firmed by optical measurements as well as comparative evaluation of the color of the pigments obtained and the glass coatings (see Table 1). The pigment with the composition 1l gives a brown-beige color of the glass layer, while the pigments 3l and 7l give blue with different intensity. The DRC is in the range 10.97 – 22.50%.

The instability of the optical characteristics of known gray pigments is explained by the unbalanced ratio between the coloring components and opacifying phases in their system, which gives rise to the appearance or domination of different chromatic tinges or colors. Undoubtedly, the nature of the opacifier used and the composition of the base glaze significantly affect the formation of the final color of the glass layer. As a result it is of interest to find a component that would secure the highest possible opacification and, in consequence, make it possible to obtain gray pigments with stable and persistent color.

The tests performed on known pigments (compositions 7l – 9l, see Table 1) showed that zinc oxide is an ineffective opacifier for obtaining gray pigment. At the same time it was determined that the total content (by weight) of the coloring components in gray ceramic pigments does not exceed 20%.

In this connection we studied zirconium, tin and titanium dioxides as opacifiers with content to 80 wt.% in the pigments. To ensure that the resulting color is black we used a ratio of the initial components that is similar to black ceramic pigment developed on the basis of open hearth slag. The experimental pigment batches were fired at 1200°C with soak-

TABLE 2. Compositions and Characteristics of the Experimental Ceramic Pigments and Glass Coatings with Pigments Added

Pigment	Content, wt.%			Pigment characteristics		Characteristics of glaze coatings	
	ZrO_2 (x_1)	TiO_2 (x_2)	SnO_2 (x_3)	Post-firing color and state (visually)	DRC, %	Color (visually)	DRC, %
1s	80	–	–	Aggregated gray powder with beige sheen	24.08	Gray with beige sheen	14.32
2s	40	40	–	Strongly aggregated gray-mustard powder	22.78	Mustard	11.20
3s	–	80	–	Gray-mustard sinter	22.20	Brown-mustard	11.12
4s	–	40	40	Gray sinter with mustard sheen	23.18	Gray-mustard	10.89
5s	–	–	80	Strongly aggregated powder with saturated gray color and rose sheen	23.36	Dark-gray with rose tinge	11.39
6s	40	–	40	Aggregated gray powder with weak rose sheen	23.70	Dark-gray with rose sheen	11.76
7s	26.67	26.67	26.67	Srongly aggregated mustard-gray powder	23.04	Mustard-gray	12.33

* Aside from the opacifying components noted the experimental pigments contained the following (wt.%): Dnepropetrovsk open hearth slag — 11.11, Cr_2O_3 — 2.78, NiO — 2.78, MnO_2 — 1.85 and CoO — 1.48.

ing time 1 h. The pigments synthesized were finely ground and introduced into the fritted base glaze [8 parts (by weight)].

The measurements of the DRC of the ceramic pigments and glass coatings with their application are presented in Table 2.

Mathematical analysis of the experimental data made it possible to obtain regression equations that adequately describe the interrelation of the DRC of the synthesized ceramic pigments and the pigment-containing glass coatings with the content of opacifiers in the pigment batches:

$$DRC_p = 24.08x_1 + 22.2x_2 + 23.36x_3 - 1.44x_1x_2 - 0.08x_1x_3 + 1.6x_2x_3 - 4.92x_1x_2x_3; \quad (1)$$

$$DRC_g = 14.32x_1 + 11.12x_2 + 11.39x_3 - 6.08x_1x_2 - 4.38x_1x_3 - 1.46x_2x_3 + 37.2x_1x_2x_3. \quad (2)$$

The measurements of the DRC of the experimental ceramic pigments and pigment-containing glaze coatings are also presented in the form of isolines, which are plotted in the corresponding concentration triangles (Fig. 1).

The experimental data (Table 2, Fig. 1) show that the formation of the gray color of the experimental ceramic pigments is achieved only by using zirconium and tin dioxides because of their high degree of inertness with respect to the coloring components in the temperature range of formation of a solid solution that is responsible for the black color component. This is evident from the visual evaluation of the color of the pigments, obtained after firing, and the values of their diffuse reflections coefficients (23.36 – 24.08%). However, titanium dioxide in the experimental ceramic pigments gives a mustard color and, in consequence, a decrease of the DRC to 22.20 – 23.18%.

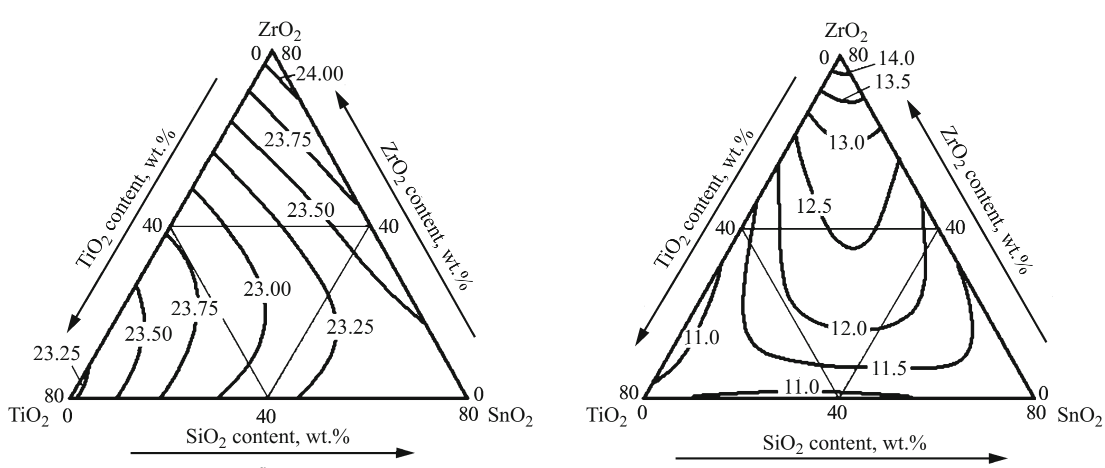

Fig. 1. DRC of the synthesized ceramic pigments (*a*) and glass coatings with pigments added (*b*) versus the composition (wt.%) of the pigment batches.

TABLE 3. Characteristics of Zirconium-Containing Ceramic Pigments and Glass Coatings with the Pigments Added

Pigment	Cobalt oxide,* parts (by weight)	Pigment characteristics		Characteristics of glaze coatings	
		Color (visually)	DRC, %	Color (visually)	DRC, %
1s-1	–	Gray with beige sheen	24.43	Gray with beige tinge	14.47
1s-2	1.5	Gray with weak beige sheen	24.00	Gray with beige sheen	13.94
1s-3	3.0	Saturated gray	22.81	Saturated gray	12.10
1s-4	4.5	Dark-gray	22.30	Dark-gray	11.44
1s-5	6.0	Dark-gray	22.17	Dark-gray with light-blue tinge	10.60

* Cobalt oxide added above 100% of the batch composition.

According to x-ray phase analysis, zirconium- and tin-containing pigments as opacifying phases contain monoclinic zirconium dioxide and tin dioxide (cassiterite) with diffraction peaks characteristic for these compounds: 3.62, 3.12, 2.80, 1.80 and 3.32, 2.62, 2.35 and 1.75 Å. A single solid solution between the spinels $MgFe_2O_4$, $MnFe_2O_4$, $CoCr_2O_4$ and $(Mg, Ni)_2MnO_4$, whose composition is similar to the base black pigment, plays the role of a carrier of the black component in such pigments.

The color of the titanium-containing pigments is largely due to the presence of titanium dioxide in the form of rutile (3.22, 2.47, 2.17 and 1.68 Å). In addition, in the process of firing the experimental pigments the titanium dioxide interacts with nickel oxide as well as with magnesium oxide, which is released during the oxidation of the magnesia-wüstite phase of the open hearth slag [10]. Thus, intense reflections corresponding to magnesium dititanate $MgTi_2O_5$ (5.03, 4.86, 3.45, 1.80 and 1.53 Å) and nickel metatitanate $NiTiO_3$ (4.61, 2.71, 1.86 and 1.73 Å) were recorded in the pigment 5s. In turn, this does not permit the formation of a solid solution with a prescribed mineralogical composition, which would secure the black component of the gray color.

The introduction of synthesized titanium-containing pigments into the composition of the base fritted glaze causes the mustard color to form in the fired glass layer, for which the DRC varies in the range 10.89 – 12.33 % (see Table 2, Fig. 1).

Only pigments obtained in the pseudobinary system ZrO_2–SnO_2 impart a gray color to the glazed coatings. Increasing the tin dioxide content intensifies the main gray color of the glass layer and imparts a rose tinge, which is accompanied by a regular drop of the diffuse reflection coefficient to 11.39%.

Evidently, the formation of a rose tinge seen in glass coatings containing tin pigments is due to the embedding of Cr^{3+} ions into the crystal lattice of their main crystalline phase — tin dioxide, which intensifies with repeated heat-treatment of such pigments during firing of the glaze itself.

These studies have established that open hearth slag can be used to synthesized gray ceramic pigments. It has been proved that zirconium dioxide, which is characterized by the highest inertness with respect to its constituent color components, is an effective opacifier. However, because of its high cost ZrO_2 must be replaced by less expensive zirconium-containing components. To this end, zirconium dioxide was replaced with zirconium silicate in the pigment 1s. In addition, cobalt oxide was introduced (to 6 parts (by weight)) in order to raise the purity of the gray color (elimination of the beige tinge). The characteristics of the ceramic pigments obtained in the process are presented in Table 3.

The experimental data, specifically, the formation of the gray color of pigments (DRC in the range 22.17 – 24.43%), show that it is expedient to replace the zirconium dioxide present in them with a less expensive component – zirconium silicate. It was also found that cobalt oxide has a positive effect on the purity and intensity of the gray color of zirconium-containing pigments. The effectiveness of CoO is observed with the introduction of 3.0 – 4.5 parts (by weight); this is supported by the character of the change in the diffuse reflection coefficient of pigments and glass coatings with the pigments added (see Table 3).

The crystal phase composition of the synthesized pigment 1s-4 (Fig. 2) is predominately represented by the mineral zircon (4.44, 3.30, 2.64, 1.70 and 1.65 Å). In addition, reflections characteristic for spinels $MgFe_2O_4$, $MnFe_2O_4$,

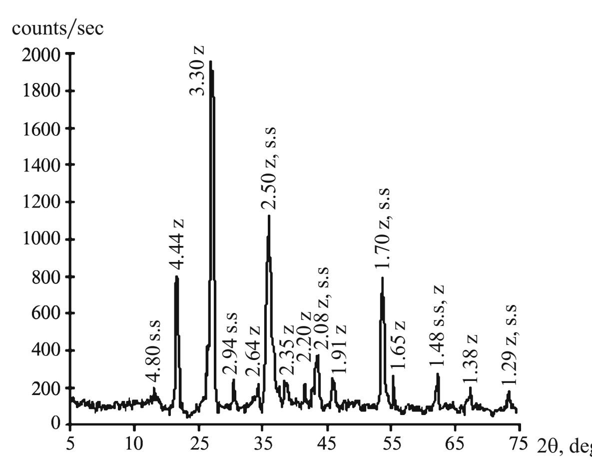

Fig. 2. Diffraction pattern of zircon-containing pigment 1s-4: z) $ZrSiO_4$; s.s.) solid solution between $MgFe_2O_4$, $MnFe_2O_4$, $CoCr_2O_4$ and $(Mg, Ni)_2MnO_4$.

$CoCr_2O_4$ and $(Mg, Ni)_2MnO_4$, forming a single solid solution, are recorded.

Subsequent increases of the cobalt oxide content (>4.5 parts (by weight)) are inadvisable, since the resulting decrease of the DRC of the pigments (from 22.30 to 22.17%) is negligible, while glaze coatings are characterized by the appearance of a light-blue tinge, which, evidently, is caused by free CoO in the phase composition of the synthesized pigment 1s-5.

The zircon-containing pigments developed have also been successfully tested in commercial glass enamel (210 N) used for enameling steel housewares (the DRC of the gray glass coatings obtained is 8.0 – 8.5%).

In summary, it was established that open hearth slag can be used as one of the main components of gray pigments. It was shown that the most effective opacifiers for gray ceramic pigments are zirconium compounds. They are characterized by inertness in the process of high-temperature synthesis with respect to different metal oxides of variable valence, which are used in such pigments, and by high resistance to dissolution in glass melts, which is what makes their optical and color indicators stable. A drawback of tin dioxide as an opacifying component in obtaining gray pigments is its proneness to coloring in rose tones even with a small amount of chromium dioxide in the system. An unfavorable property of titanium dioxide as an opacifier in gray pigments is that at high synthesis temperatures (>900°C) it transitions into a rutile phase (color from cream to yellow). Titanium dioxide also manifests quite high activity with respect to different components of pigments, thereby making it impossible for the prescribed crystalline phases responsible for the black component of the color to form.

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